Determination of an Equilibrium Constant

Chemical reactions occur to reach a state of equilibrium. The equilibrium state can be characterized by quantitatively defining its equilibrium constant, K. In this experiment, you will determine the value of K for the reaction between iron (III) ions and thiocyanate, SCN^-. Ferric ions react with thiocyanate ions to form iron (III) thiocyanate, $FeSCN^{2+}$, which is a stable complex ion with a blood-red color:

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq, \text{deep red})$$

The equilibrium constant expression for this reaction is

$$\mathbf{K_C} = [FeSCN^{2+}]/([Fe^{3+}]\bullet[SCN^-])$$

To find the value of K, which depends only on temperature, it is necessary to determine the molar concentration of each of the three species in solution at equilibrium. You will use a colorimeter to help you measure the concentrations. Solutions of iron (III) ions are weakly colored and thiocyanate ion is colorless, so the primary absorber in a mixture of these components is $FeSCN^{2+}$. This ion obeys Beer's law (A = abC) over a fairly wide range of concentrations, allowing measurement of its concentration in various equilibrium mixtures. The red colored solutions absorb blue light very well, which is why we are using 470 nm. From its measured equilibrium concentration and the initial concentrations of Fe^{3+} and SCN^-, it is possible to determine the concentrations of all three components, and from them, the equilibrium constant for the reaction.

The iron (III) ion introduces a complication because of its reaction with water to form iron (III) hydroxide, which is insoluble in water:

$$Fe^{3+}(aq) + 3H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3H^+(aq)$$

To avoid precipitation of iron (III) hydroxide, excess nitric acid (HNO_3) will be included in all solutions, to shift this equilibrium far to the left. Because neither hydrogen ions nor nitrate ions are components of the iron (III) thiocyanate equilibrium, nitric acid does not affect the equilibrium position of the reaction that produces $FeSCN^{2+}$.

In Part 1 of this experiment, you will prepare a series of **calibration solutions** having known concentrations of the iron (III) thiocyanate ion. To do so, you will use a small, known amount of thiocyanate, and a large excess of Fe^{3+} to drive the reaction to the right, incorporating all of the thiocyanate into $FeSCN^{2+}$. In each of these solutions, therefore, the equilibrium concentration of $FeSCN^{2+}$ equals the initial concentration of SCN^-. You will determine the absorbance of each solution, prepare a Beer's law plot, and obtain the equation of the line relating **A** and **C**.

In Part 2 of the experiment, you will analyze a solution of unknown $[SCN^-]$ by using the same procedure that you followed in Part 1. In this manner, you will determine the molar concentration of the SCN^- solution.

In Part 3, you will prepare five mixtures with known initial concentrations of iron (III) and thiocyanate ion. You will determine the absorbance of each mixture after it reaches equilibrium, and then use the equation of your Beer's law plot (Part 1) to determine the concentration of $FeSCN^{2+}$ in each equilibrium mixture. Finally, from the measured $[FeSCN^{2+}]$, and the known initial $[Fe^{3+}]$ and $[SCN^-]$, you will determine the equilibrium constant $\mathbf{K_C}$ for this reaction.

In the five different equilibrium solutions, the equilibrium concentrations, and hence the equilibrium positions, are different. But your measured values of the equilibrium constant should be the same, within expected experimental variation (within one power of 10).

Materials

Computer	CBL	Colorimeter
Plastic Cuvettes	Test Tubes	Thermometer
0.0020 M KSCN	0.0020 *M* $Fe(NO_3)_3$ (in 1.0 *M* HNO_3)	0.0020 *M* $Fe(NO_3)_3$ (in 1.0 *M* HNO_3)
10 mL Graduated Cylinder	Stirring Rod	small beakers

Pre-Lab Exercise

For the solutions that you will prepare in Step 2 of Part 1 below, calculate the [$FeSCN^{2+}$]. Assume that all of the SCN^- ions react. In Part 1 of the experiment,

$$\text{mol of } SCN^- = \text{mole of } FeSCN^{2+}$$

Thus, the calculation of [$FeSCN^{2+}$] is:

$$\text{mol } FeSCN^{2+}/\text{L of total solution}$$

Record these values in the data table in your notebook. (Note: You can just show one example calculation and do the rest in an Excel spread sheet if you want.)

Methods

Part I: Prepare and Test the Standard Solutions

1. Obtain and wear goggles.

Note: There are two different concentrations of $Fe(NO_3)_3$ in 1.0 *M* HNO_3. Be certain that you are using the correct solution for each step below! Nitric acid solution should also be handled with care. It will stain your skin.

2. Label the five beakers 1-5. Obtain the appropriate volumes of 0.200 *M* $Fe(NO_3)_3$ and 0.0020 *M* KSCN according to the chart below. The two solutions are located in burets for easy dispensing. Also measure and record a temperature for one of the solutions to use as the temperature for the equilibrium constant, K.

Beaker Number	0.200 *M* $Fe(NO_3)_3$ (mL)	0.0020 *M* KSCN (mL)	H_2O (mL)
1	5.0	0.0	45.0
2	5.0	2.0	43.0
3	5.0	3.0	42.0
4	5.0	4.0	41.0
5	5.0	5.0	40.0

3. Set up the data collection system as you did in the previous lab. Be sure to calibrate the colorimeter, and set it to read absorbance at 470 nm. For this lab your data collection mode will just be SINGLE POINT.

4. Collect and record the absorbance data for the standard solutions. **Note: Take readings within 4 minutes of preparing the mixtures.** Make sure to rinse the cuvette twice with ~1 mL of amounts of each solution before you take an absorbance reading. Also be sure to wipe down the outside of the cuvette with a KimWipe® before taking absorbance readings. Record the absorbance values for all trials in your lab notebook. Remove and clean the cuvette.

Part II: Test an Unknown Solution of SCN^-

1. Obtain about 10 mL of the unknown SCN^- solution. Use a pipet to measure out 5.0 mL of the unknown into a clean dry 100 mL beaker. Add precisely 5.0 mL of 0.200 *M* $Fe(NO_3)_3$ and 40.0 mL of distilled water to the beaker. Stir the mixture thoroughly.

2. Using the solution from the beaker, rinse the cuvette twice with ~1 mL of amounts, fill the cuvette ¾ full, and take an absorbance reading in the colorimeter. Also be sure to wipe down the outside of the cuvette with a KimWipe® before taking absorbance readings. Record the absorbance value in your lab notebook. Remove and clean the cuvette.

Part III: Prepare and Test Equilibrium Systems

1. Prepare five test tubes of solutions according to the chart below. Test the absorbance values of each mixture and record the test results in your data table. **Note:** You are using 0.0020 *M* $Fe(NO_3)_3$ in this test.

Test Tube Number	0.0020 *M* $Fe(NO_3)_3$ (mL)	0.0020 *M* KSCN (mL)	H_2O (mL)
1	3.0	0.0	7.0
2	3.0	2.0	5.0
3	3.0	3.0	4.0
4	3.0	4.0	3.0
5	3.0	5.0	2.0

2. To get good data for the calculation of *K,* you must determine the net absorbance of the solutions in test tubes 2-5. To do this, subtract the absorbance reading for test tube 1 from the absorbance reading of test tubes 2-5, and record these values as net absorbance in your data table.

Data Analysis

1. Calculate the linear regression (best-fit line) equation of absorbance vs. concentration for the five standard solutions and record it in your data table. Use the best-fit line and the absorbance reading for your unknown solution to determine [SCN^-].

2. Compare your experimental [SCN^-], of your unknown, with the actual [SCN^-]. Suggest reasons for the disparity.

3. Use the net absorbance values, along with the best-fit line equation of the standard solutions in Part I to determine the [$FeSCN^{2+}$] at equilibrium for each of the mixtures that you prepared in Part III. You can show one example calculation for this and just show the other three calculated values in a data table.

4. Calculate the equilibrium concentrations for Fe^{3+} and SCN^- for the mixtures in test tubes 2-5 in Part III. You can show one example calculation for this and just show the other three calculated values in a data table.

5. Calculate the value of *K* for the reaction. Explain how you used the data to calculate *K* for the reaction.